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Assessment of Volatile Organic Emissions from a Petroleum Refinery Land Treatment Site

Radian Corp., Austin, TX

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Assessment of Volatile Organic Emissions from a Petroleum Refinery Land Treatment Site

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ABSTRACT

A field assessment was performed to measure the emissions of volatile organics from a petroleum refinery land treatment site. As part of this study, the emissions of total volatile organics from surface-applied and subsurface-injected oily sludge were measured over a 5-week period. The effect of soil tilling on the emissions also was monitored.

Volatile organics emission rates were measured using the emission isolation flex chamber method. Soil samples were collected during the test periods to determine soil properties, oil levels and microbe count. Soil surface and ambient temperatures, both inside and outside the flux chambers, were measured throughout the test periods.

INTRODUCTION

The U.S. EPA currently is developing background information on air pollutants at hazardous waste treatment, storage and disposal facilities (TSDFs) to provide supporting data for setting standards as necessary under Section 3004 of RCRA as amended in 1984. This regulatory development is the responsibility of the Office of Air Quality Planning and Standards (OAQPS). The U.S. EPA Hazardous Waste Environmental Research Laboratory-Cincinnati (HWERL) has the responsibility of providing technical support to OAQPS in the area of atmospheric emissions determination from hazardous waste management.

In order to assess emissions from hazardous waste TSDFs, a field study was performed at a land treatment facility located at a large West Coast petroleum refinery. This study was intended to: (1) measure the total volatile organics emission rates from surface- and subsurface-applied oily refinery sludge and (2) to determine how emissions of volatile organics varied with time. Based on these measurements the total emissions over a 5-week period were estimated.

Little work has been performed to characterize volatile organic emissions from large full-scale land treatment sites. The study approach and selected results are summarized in this paper. A more detailed description of the work and its limitations in included in a previous U.S. EPA report.[1] The emissions of individual measured compounds are provided in that U.S. EPA report.

DESCRIPTION OF THE TEST SITE

The test site was located at a large West Coast refinery. The land treatment area covers approximately 42,000 m^2 (10 acres). Three test plots, each approximately 420 m^2 (0.1 acre) in area, were located side-by-side at one corner of the facility. The area containing the test plot has been in land treatment service for several years.

During normal operation, sludge from refinery operations is collected and stored in a fixed-roof tank at the land treatment area. The sludge is injected subsurface using an 8,000 l (50-barrel) capacity injector vehicle equipped with four separate injector tines. The injector vehicle consists of a tractor and an 8,000 l (50-barrel) capacity tank trailer. The tines are attached to the tank trailer. The waste is injected 15 to 28 cm below the surface and immediately disked by a disk unit pulled behind the injector vehicle. The area is cultivated with a disk and/or rototiller several times per week until the next sludge application.

According to the operators of this facility, the annual application rate at this site is about $5.4 - 9.1 \times 10^6$ kg/year, and the individual application rates are typically about 16 l/m^2 (400 barrels/acre). The sludge typically consists of 50 to 75% DAF/API separator float, 20 to 30% API separator sludge and about 5% miscellaneous oily waste. The soil is irrigated periodically to maintain proper soil moisture content.

EXPERIMENTAL APPROACH

The experimental design, sampling techniques, analytical methods and test procedures are summarized below.

Experimental Design

The experimental design of this program was developed to obtain data of sufficient accuracy to fulfill the major objectives of the study. The primary emphasis of the program was on obtaining volatile organics emission rate measurements. The test design was a synthesis of two sampling strategies for obtaining emission measurements: totally randomized sampling over the test plots and semi-continuous sampling at a single location in each plot.

To provide an overall estimate of the volatile organics emission rate for a total test plot area, a number of measurements at randomly selected points must be performed. One method of ac-

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16. ABSTRACT

A field assessment was performed to measure the emissions of volatile organics from a petroleum refinery landtreatment site. As part of this study, the emissions of total volatile organics from surface-applied and subsurface-injected oily sludge were measured over a five week period. The effect of soil tilling on the emissions was also monitored.

Volatile organic emission rates were measured using the emission isolation flux chamber method. Soil samples were collected during the test periods for determination of soil properties and oil levels. Soil surface and ambient temperatures inside the flux chambers were also measured throughout the test periods to determine their influence on emission rates.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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complishing this is to divide the area into discrete segments and then randomly select segments to be tested. On the other hand, the best strategy for examining the change in emission rate with time is the repeated sampling of a limited number of points over a period of time.

Three test plots were used in this study. Sludge was surface-applied to one plot (Plot A) and subsurface-injected at another plot (Plot C). In between these two plots was a third plot (Plot B) with no sludge applied. Plot B served as a baseline or control plot. Each plot was approximately 420 m² (0.1 acre) in size, and each was divided into 21 segments, as shown in Figure 1, to provide for randomized sampling.

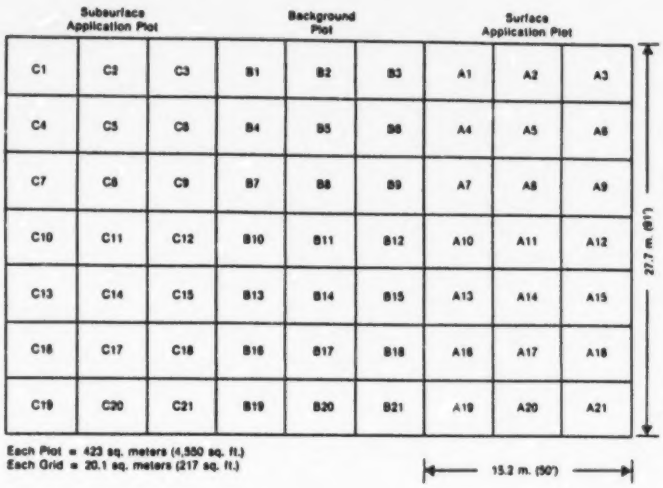
Subsurface Application Plot
Background Plot
Surface Application Plot
C1 C2 C3 B1 B2 B3 A1 A2 A3
C4 C5 C6 B4 B5 B6 A4 A5 A6
C7 C8 C9 B7 B8 B9 A7 A8 A9
C10 C11 C12 B10 B11 B12 A10 A11 A12
C13 C14 C15 B13 B14 B15 A13 A14 A15
C16 C17 C18 B16 B17 B18 A16 A17 A18
C19 C20 C21 B19 B20 B21 A19 A20 A21
27.7 m. (91')
Each Plot = 423 sq. meters (4,550 sq. ft.)
Each Grid = 20.1 sq. meters (217 sq. ft.)
15.2 m. (50')

Figure 1
Test Plot Grid Assignment for Assessment of Emissions from Land Treatment of Petroleum Wastes

Sampling schedules for each plot were developed for each separate day of sampling. Each sampling day was divided into two parts. During each half day, one sampling crew made measurements at the surface-applied plot, and the other crew performed similar measurements at the subsurface injected plot. Each crew performed emission measurements at two separate control points, at two randomly selected points in their assigned plot and at one randomly selected point in the control plot. Random number tables were used to select the order of sampling, the crew used on each plot and the equipment set used by each crew. The sampling order for composite soil samples, soil cores, gas samples and their associated duplicates within a given plot were also randomly selected. A typical daily sampling schedule is shown in Table 1.

Table 1
Typical Daily Sampling Schedule

Approximate Time	Grid Point[a]	Flux Chamber Sampling: Crew ID	Flux Chamber Sampling: F/C ID[b]	Samples Collected: Canister	Samples Collected: Soil	Samples Collected: Syringe	Comments
	TEXT PLOT A	DATE:	11/09/84	APPLICATION METHOD:		SURFACE	
0800	——	002	003	-	-	X	QC
0845	A07[c]	002	003	-	X	X	
0930	B03	002	003		X	XX	
1015	A05	002	003	-	-	X	
1100	A19[c]	002	003	X	X	X	
1145	A01	002	003	-	-	X	
1230	——	002	003	-	-	-	TIII
1400	A07[c]	002	003	X	-	X	
1445	A19[c]	002	003	X	-	X	
1530	B14	002	003	X	-	X	
	TEST PLOT A	DATE:	11/09/84	APPLICATION METHOD:		SUBSURFACE	
0800	——	001	002	-	-	X	QC
0845	C11[c]	001	002	X	X	X	
0930	C13	001	002	-	-	X	
1015	C14	001	002	-	-	X	
1100	C15[c]	001	002	-	-	XX	
1145	B15	001	002	-	-	X	
1230	——	001	002	-	-	-	TIII
1315	C15[c]	001	002	X	-	X	
1400	C11[c]	001	002	-	-	X	
1445	C04	001	002	-	X	X	
1530	C06	001	002	X	X	X	
1615	B03	001	002	-	-	X	

a. Prefix A, B, C refers to plot A (surface applied), plot B (background or control plot), and plot C (subsurface applied).
b. F/C = flux chamber
c. Control points

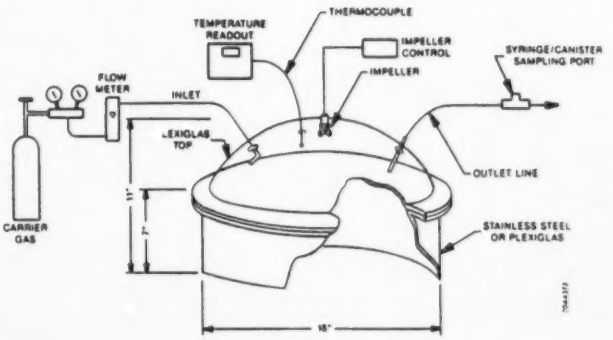

Figure 2
Cutaway Side View of Emission Isolation Flux Chamber and Sampling Apparatus

Sampling Procedures

The main sampling technique employed at this site involved the direct measurement of emissions using the emission isolation flux chamber. The enclosure emission measurement approach has been used by others to measure emission fluxes of sulfur and volatile organic species.[2,3,4]

A diagram of the flux chamber is shown in Figure 2. The flux chamber was placed on the emitting surface. Clean, dry air was passed through the chamber at a controlled and measured rate. The concentration of the specie(s) of interest was measured at the outlet of the chamber. The emission rate of the measured specie(s) from the enclosed surface was then calculated from the flow rate and concentration in the gas.

The flux chamber encloses a surface area of 0.13 m² and has a volume of 0.031 m³. The sweep air flow rate was 0.003 - 0.005 m³/min. Air samples were collected from the outlet gas line using both gas-tight syringes (for on-site analyses) and evacuated stainless steel canisters (for off-site analyses).

Liquid grab samples of the sludge and of the service water used to irrigate the soil were collected. Sludge from two tank trucks was transferred to the application vehicle (tractor) and applied to the soil. Each tank truck held two application tractor loads. After the first load was transferred from the tank truck to the application tractor, 4-6 sample containers were filled with sludge from the tractor. The samples were collected consecutively, while the tractor tank was full, from a gravity-fed line. While two tractor

loads were required to empty each tank truck, samples were collected after only one of the two transfers from each tank truck load. One service water sample was collected from the plant service water line to determine the concentration of organics in this water which the facility applies as part of its site management technique.

Two types of solid samples were collected: soil composites and undisturbed soil cores. Both types of samples were collected immediately adjacent to points where flux chamber measurements were made. Soil composites were used in the determination of oil and moisture contents. These samples were collected using a hand auger and boring to a depth of 30 to 40 cm. The undisturbed soil samples were used for determining the physical properties of the soils. They were obtained by driving a brass sleeve approximately 20 cm into the ground, removing the sleeve and capping both ends.

Type K thermocouples were used to monitor the air and soil temperatures both inside and outside each flux chamber. Two separate thermocouples were used to measure soil surface temperatures inside and outside the flux chamber. Each was placed in the ground to a depth of 1.3 to 1.9 cm.

Analytical Procedures

The on-site analyses were limited to gas-phase analyses of the air samples collected in gas-tight syringes from the outlet of the flux chambers. A Byron Instruments Model 401 Total Hydrocarbon (THC) Analyzer was used to determine the concentrations of total hydrocarbons (THC), CO_2 and methane in the effluent air samples from the flux chamber.

The off-site analyses included the chemical speciation of the flux chamber air samples collected in stainless steel canisters and of the liquid sludge and water samples collected at the land treatment site. The oil, moisture and microbe levels in the soil also were determined, as were the physical properties of the soil samples.

Chemical speciation of the air and liquid samples for C_2 and C_{10} hydrocarbons was performed with a Varian 3700 Gas Chromatograph. The chemical species were cryogenically concentrated to increase the sensitivity of the analyses. Liquid samples were analyzed using a purge-and-trap technique modified to utilize the cryogenic trap. For both air and liquid samples, total volatile organics concentrations were obtained as the sum of the species concentrations.

The oil, water and solids contents of the sludge samples were determined by solubilizing the oil and water in the waste with tetrahydrofuran (THF). This liquid phase was then separated from the insoluble solids. Residual solids were weighed, and the amount of water in the THF was determined by Karl Fischer titration. The oil content was calculated by difference. The oil and grease content of the soil samples was determined using U.S. EPA Method 413.1. Standard methods were used to determine the bulk density, particle density, total porosity, moisture content and particle size distribution.

Sludge Application

The sludge was applied as evenly as possible to the surface-applied Plot A (SA plot) and to the subsurface-injected Plot C (SSA plot). The application tractor started injecting sludge at grid point (GP) C19 (Fig. 1) and moved across Plot C from GP C19 through GP C21. The injector then was lifted above the soil, and the tractor proceeded across Plot B (control plot) from GP B19 across GP B21. No sludge was applied to Plot B. Sludge then was allowed to flow from the raised injector tines onto the surface of Plot A as the tractor passed across it from GP A19 through GP A21. The tractor then made a U-turn and returned across Plots A, B and C while applying sludge. Several application passes were made to complete the application to the entire area of Plots A and C. Three complete tractor loads and part of another were required. The average waste loading was 1.4×10^4 kg/plot. All three plots were tilled with a disk tiller pulled behind the tractor during the sludge application.

Emission sampling with the flux chambers was started immediately after application and continued for 4 days. Emission sampling was performed during two other 4-day periods in the 3rd and 5th weeks following application. Each plot was tilled 2-3 times per week during the 5-week test period. The plots also were irrigated with water once between the first and second sampling periods and three times between the second and third sampling periods. The complete tilling and irrigation schedule for the test period is summarized in Table 2.

Table 2
Tilling Schedule for Land Treatment Facility During Test Study

Date	Tilling Time	Hours from Start[a]	Activity
10-10-84	0950-1030	0	Apply waste and Till
10-12-84	1224-1258	50.5	Till
10-15-84	0930-1100	120.5	Till and Irrigate
10-16-84	1300-1400	147.5	Till
10-18-84	0800-0930	191	Till
10-19-84	1300-1430	220	Till
10-24-84	1222-1235	338.5	Till
10-26-84	1218-1233	386.5	Till
10-29-84	0815-0930	455	Till
10-30-84	0900-1100	480	Till and Irrigate
10-31-84	1000-1100	504.5	Till
11-01-84	0900-1100	528	Till and Irrigate
11-02-84	0900-1030	552	Till
11-05-84	1300-1430	628	Till and Irrigate
11-09-84	1225-1245	722.5	Till
11-12-84	1047-1110	793	Till

a. Rounded off to nearest 1/2 hour.

SAMPLING AND ANALYSES RESULTS

The results of the sample analyses for the gas, liquid and soil samples are summarized below.

Gas Samples

The results of the on-site Byron THC analyses agreed quite well with the off-site Varian 3700 analyses. The results were correlated with a correlation coefficient of 0.977. The Varian GC generally gave slightly higher concentrations, with an average difference of 13.8% between the Byron and Varian instruments.

No methane was detected in any of the on-site samples analyzed with the Bryon 401, which is capable of detecting methane at levels of 1 ppm.

The CO_2 concentrations in the on-site gas samples were found to range from about 50 ppm to almost 500 ppm. Most values fell between 100 and 300 ppm. Background CO_2 levels, as determined by sealing the bottom of the flux chambers and passing air through them, were in the range of 10 to 200 ppm.

Liquid Samples

The sludge samples were analyzed several times to define the sludge nonhomogeneity and obtain an average value for the level of volatile organics. The analyses were performed over a period of several months (during which the samples were kept under refrigeration). The measured volatile organics content of the sludge, as determined with the purge-and-trap technique, ranged from 4,250 to 16,600 μg/g. Most volatile organics concentrations were between 4,000 and 6,000 μg/g, with the mean value being 7,800 μg/g. The variability was believed to be at least partially attributable to the difficulty of obtaining a representative sample in small quantities for analysis. The sludge volatile organic component was made up principally of paraffins (average concentration = 3,600 μg/g), olefins (1,200 μg/g) and aromatics (2,900 μg/g). The remainder of the volatiles were halogenated and oxygenated hydrocarbons and unidentified organics. From the characterization tests, the sludge was found to consist of 3.9 to 4.5% solids, 57.5 to 59.1% water and 37.0 to 38.0% oil.

The sample of service water used to irrigate the soil was also analyzed for volatile organics to determine whether this water could be a significant source of volatile organics (this sample was kept under refrigeration and analyzed approximately 3 months after collection). The volatile organics content was found to be 0.089 mg/l. The total amount of volatile organics applied with the water over the duration of the test was estimated to be about 0.03 kg/plot. This amount is equivalent to less than 0.5% of the volatile organics applied in the sludge.

Soil Samples

The mean values for the physical properties determined for the soil samples are summarized in Table 3. Also included are the mean moisture content and oil/grease levels for the collected samples. The results are summarized for two of the three sampling periods.

Table 3
Mean Soil Properties

Test Week	Particle Density (g/cm³)	Moisture Content (wt %)	Bulk Density (g/cm³)	Porosity, (%)	Oil and Grease (mg/g)
1	2.50	7.40	1.21	52	64
3	2.54	7.89	1.42	44	56

STATISTICAL ANALYSES OF THE DATA

A statistical analysis was performed primarily to investigate the effects of time, temperature inside the chamber (soil and air), plot samples, location within each plot and chamber shading on emission rates. The frequency distribution of the emission rate data was highly skewed and a log normal distribution was used to model the frequency distribution of emission rates. To determine whether measurable differences existed among the emission rates from the test plots, an analysis of covariance was performed. The analysis of covariance technique eliminates the variation in emission rates due to other variables such as time, temperature (inside the chamber) and chamber surface shading. In this way, the average emission rates for the test plots can be directly compared. A discussion of the analysis of covariance can be found in Brownlee.[3]

The statistical analysis indicated that the emission rates were significantly affected by test plot and elapsed time. The results of the statistical analysis are summarized in Table 4. Soil or air temperatures within the chamber were marginally significant. None of the other variables were found to have a significant affect on the emission rates.

Table 4
Components of Variability

Source of Variability	Variance Component[a]	Percent of Total Variance[b]	Percent of Total Minus Temporal Variance
Temporal (day-to-day)	58.3	63.0	—
Air Temperature in Chamber	3.3	3.6	9.6
Plot	28.1	30.4	82.2
Sampling Location (within the plot)	1.4	1.5	4.1
Surface Chamber Shading	0.42	0.4	.2
Sampling/Analytical	1.0	1.1	2.9
Total	92.5	100	100

a. Variance components are equal to standard deviations squared and thus have units which are the squares of that used for the log-emission rates $(\mu g/m^2\text{-sec})^2$.

b. Relative contribution of parameters to the total variance.

The oil and moisture contents of the soil samples were examined to determine whether there was any significant change with time in these parameters. There appeared to be little change in the oil content of the soil over the duration of the test. The moisture content of the soil appeared to decrease by about 14 to 40% over the test period. Both changes were so small that no correlation with emission rates could be determined.

MEASURED VOLATILE ORGANICS EMISSION RATES

The volatile organics emission rates were examined with respect to elapsed time since application, ambient conditions at the time of sampling and tilling activities.

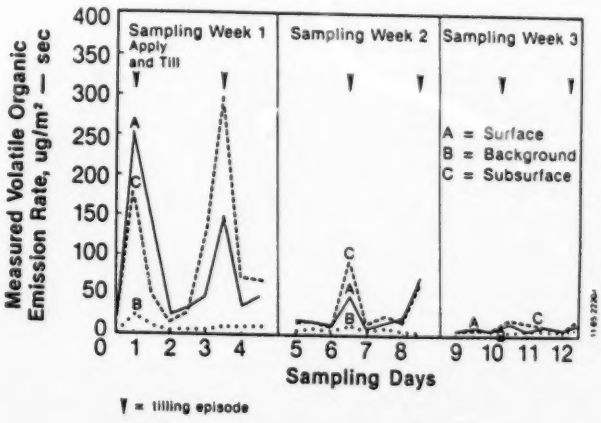

Figure 3
Measured Emission Rates as a Function of Time Elapsed Since Sludge Application

Table 5
Average Measured Emission Rates by Plot by Half-Day

Sampling Day	Date	Emission Rate ($\mu g/m^2$-s) A Plot (Surface)	B Plot (Background)	C Plot (Subsurface)	Comments
0	10-09-84	1.88	1.48	1.95	
1	10-10-84	249	24.7	176	
	10-10-84	142	10.0	52.8	
2	10-11-84	22.5	4.09	13.8	early start
	10-11-84	32.6	5.11	26.5	
3	10-12-84	48.2	4.09	120	
	10-12-84	146	9.93	295	†III
4	10-13-84	33.4	8.18	71.2	
	10-13-84	46.3	8.86	67.4	
5	10-23-84	16.6	2.71	12.4	
	10-23-84	15.0	6.13	15.1	
6	10-24-84	8.04	2.73	10.1	
	10-24-84	49.1	10.0	91.3	†III
7	10-25-84	6.41	2.04	12.1	early start
	10-25-84	13.5	5.80	22.0	
8	10-26-84	21.8	1.32	13.0	
	10-26-84	71.1		59.3	†III
9	11-08-84	2.56	2.59	2.93	
	11-08-84	7.25		5.76	
10	11-09-84	1.24		3.94	
	11-09-84	12.34	1.22	16.2	†III
11	11-10-84	2.49	1.39	11.3	
	11-10-84	6.4	1.43	7.13	
12	11-12-84	2.97	1.19	4.06	
	11-12-84	10.5	4.42	16.2	†III

Each Plot Area = 423 m^2

Table 6
Cumulative Measured Emissions

Sampling Day	Emission Rate (kg) A Plot (Surface)	B Plot (Background)	C Plot (Subsurface)	Comments
1	1.327	0.1317	0.938	
	2.084	0.1850	1.219	
2	2.204	0.2068	1.293	early start
	2.378	0.2340	1.434	
3	2.634	0.2558	2.074	
	3.413	0.3088	3.646	†III
4	3.591	0.3524	4.026	
	3.837	0.3996	4.385	
5	3.926	0.4140	4.451	
	4.006	0.4467	4.531	
6	4.049	0.4613	4.585	
	4.310	0.5146	5.072	†III
7	4.345	0.5254	5.136	early start
	4.417	0.5563	5.254	
8	4.533	0.5634	5.323	
	4.912		5.639	†III
9	4.925	0.5772	5.655	
	4.964		5.685	
10	4.971		5.706	
	5.036	0.5837	5.793	†III
11	5.050	0.5911	5.854	
	5.084	0.5987	5.892	
12	5.100	0.6051	5.914	
	5.156	0.6286	6.000	†III

Each Plot Area = 423 m^2

Effect of Elapsed Time from Application on Emission Rates

The measured emission rates for the three plots are shown as functions of elapsed time in Figure 3. The average measured emission rates are summarized for each half-day of sampling. These rates are tabulated in Table 5. The first point (Day 0) was measured before sludge application. The tabulated values and the figure show the approximately exponential decline in emission rates with time elapsed from application (and, to some extent, elapsed time from tilling episodes). The emission rates from the control Plot B remained substantially below those of the test plots throughout the duration of the testing.

The cumulative measured volatile organics emissions are summarized in Table 6 and shown graphically in Figure 4. An approximately exponential decline in the emission rates is evident.

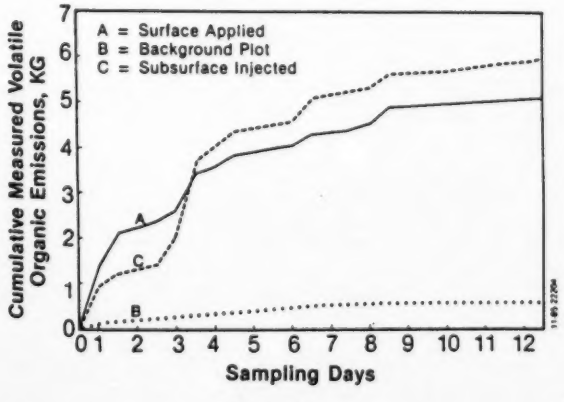

Figure 4
Cumulative Measured Emissions as a Function of Sampling Day
(includes only measured rates for days on which sampling was performed)

Effect of Tilling on Emission Rates

Tilling of the soil had a significant effect on the emission rate. The effect can be seen clearly in Figure 3 as spikes in the emission rates immediately after tilling. The percentage increase in average emission rates by half-day immediately following tilling episodes is shown for each plot in Table 7. The five tilling episodes for which emission measurements were made were distributed among the three sampling periods.

Table 7
Increase in Emission Rate Due to Tilling

Observed Tilling Episode	Percent Increase in Emission Rate A Plot (Surface)	B Plot (Background)	C Plot (Subsurface)
1	303	243	246
2	611	366	904
3	326	0[a]	456
4	995	0[a]	411
5	354	371	399

a. Incomplete data set

ESTIMATED EMISSION RATE FOR THE 5-WEEK TEST PERIOD

The emission rates and cumulative emissions for the entire 5-week test period were estimated from the measured rates. The following assumptions were made to estimate the total emissions:

- Tilling had no effect on emission rates beyond 6 hours after tilling occurred
- Each day had 12 hours of cooler temperatures (night)

The emission rates were estimated for three distinct times during each sampling period. These were: (1) nighttime, (2) non-tilling daytime and (3) tilling daytime. The nighttime emissions for each sampling period were estimated from the emission rate data obtained during the early morning hours of that period. The tilling and non-tilling day emissions for each sampling period were derived from the appropriate emission rate measurements. Emissions for the interval between sampling periods were obtained by interpolation among the three emission rates for the three sampling periods. Summing all the night-time, non-tilling daytime and tilling daytime emissions, the total emissions for each of the plots for the 5-week period were estimated to be:

Plot A (surface applied):	33.3 kg
Plot B (control):	5.2 kg
Plot C (subsurface inj.):	39.0 kg

The estimated total emissions per plot per week are shown in Figure 5.

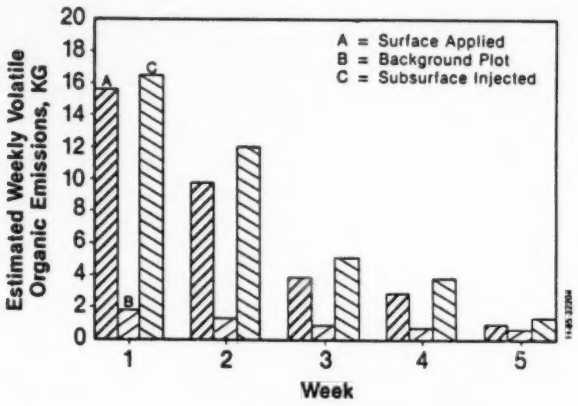

Figure 5
Total Estimated Weekly Emissions from Each Plot

CONCLUSIONS

The results of the detailed sampling and analysis of total volatile organic emissions from this land treatment facility indicate that emissions from both surface-applied and subsurface-injected waste varied in a similar, approximately exponentially decaying manner over the 5-week period of this test. This result is in agreement with the predictions of the Thibodeaux-Hwang emissions model for surface-applied plots.[6]

Also, the effect of tilling is similar for both application methods. Tilling resulted in a 2- to 10-fold increase in the emission rates. A large portion of the 5-week cumulative emissions from both plots is due to emissions which occurred within 4 hours after tilling was performed. The magnitude of emissions which occurred immediately after tilling decreases from tilling event to tilling event approximately in proportion to the decrease in emissions during non-tilling periods.

Based on a statistical analysis of the emissions, it was found that the emission rates were significantly affected by the elapsed time. Soil and air temperatures within the chamber were marginally significant. None of the other variables that were monitored were found to have a significant effect on the emission rates.

NOTICE

The information in this document has been funded wholly or in part by the U.S. EPA under contract to Radian Corporation. It has been subject to the Agency's peer and administrative review, and it has been approved for publication. Mention of tradenames or commercial products does not constitute an endorsement or recommendation for use.

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